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COMBUSTION MECHANISM OF AMMONIUM AND  
HYDRAZONE SALTS

G. B. Manelis, et al

Foreign Technology Division  
Wright-Patterson Air Force Base, Ohio

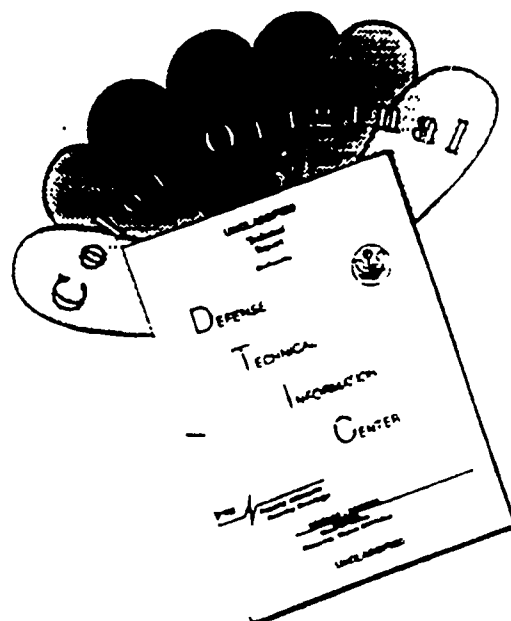
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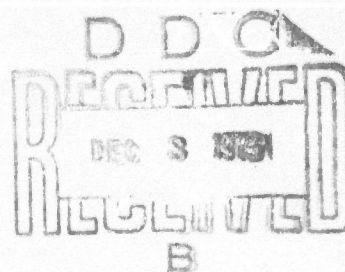
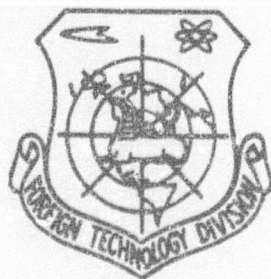
## FOREIGN TECHNOLOGY DIVISION



COMBUSTION MECHANISM OF AMMONIUM AND  
HYDRAZONE SALTS

by

G. B. Manelis, V. A. Strunin



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Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

\* ye initially, after vowels, and after ъ, ь; e elsewhere.  
 When written as ѣ in Russian, transliterate as yě or ë.  
 The use of diacritical marks is preferred, but such marks  
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## COMBUSTION MECHANISM OF AMMONIUM AND HYDRAZONE SALTS

G. B. Manelis, and V. A. Strunin

Chernogolovka

Many salts of ammonia and hydrazone (for example, perchlorates, nitrates) are capable of self-contained combustion. A characteristic feature of these compounds is the rather high rate of reaction of the decomposition in the condensed phase and the capacity for vaporization. *The transition decreases the reaction kinetics.*

The kinetics of the reactions in the basic features is expressed by the following scheme [1, 2]:

the initial stage is the reversible transfer of the proton



The products of dissociation are vaporized (endothermic process) or decomposed (exothermic process).

The rate of reaction of the decomposition which limits the process can depend in general both on the concentration of R (hydrazine) and the concentration of HX (acid):



$$w_{yx} = K [R]_k^n [HX]_k^n. \quad (1)$$

The solubility of R and HX in the initial substance is different and determined by the constant of equilibrium  $K_1 = [R]_k [HX]_k$  and the equation of the conservation of the mass of the substance with its dissolution and vaporization

$$([R]_k + [RH]_k) V_k + [R]_r V_r = ([HX]_k + [X]_k) V_k + [HX]_r V_r, \quad (2)$$

where V is the volume, and the subscripts k and r denote the condensed and gas phase.

The concentrations of components in the condensed phase are proportional to concentrations in the gas phase (Henry's law)

$$[R]_k = K_R RT [R]_r; \quad [HX]_k = K_{HX} RT [HX]_r, \quad (3)$$

where  $K_R$  and  $K_{HX}$  are constants of solubility

From equation (2) it follows that if  $[HX]_k$ , owing to the great solubility of this product, exceeds  $[R]_k$ , then for preserving the balance  $[HX]_r$  should be less than  $[R]_r$ . Since the quantity of vapor carried away by the finite products of decomposition depends on their volume and, consequently, on the pressure, then  $[R]_k$ ,  $[HX]_k$  and the rate of reaction will also be changed with pressure.

Let us examine one of the simple cases when

$$w_{yx} = K [HX]_k^2. \quad (4)$$

Taking into account that

$$V_r/V_k = [m_c \tau_c + m_p(1 - \tau_c)] pRT/p; \quad (5)$$

$$p = \left[ 1 + \frac{m_p(1 - \tau_c)}{m_c \tau_c} \right] p_c; \quad (6)$$

$$[RH^+]_k = [X^-]_k, \quad (7)$$

from equation (2)

$$[HX]_k = \frac{K_R K_{HX}}{K_R} \cdot \frac{1 + K_{HX}^{-1} [m_p^{-1} p + (m_c^{-1} - m_p^{-1}) p_c]}{1 + K_{HX}^{-1} [m_p^{-1} p + (m_c^{-1} - m_p^{-1}) p_c]}, \quad (8)$$

where

$\eta$  - portion of vaporized substance;

$m_p$  and  $m_c$  - number of moles formed with the decomposition and evaporation of one mole of substance;

$\rho$  - density of the condensed phase;

$p$  - pressure;

$p_c = B \exp(-L/RT)$  - pressure of the saturated vapor.

The rate of combustion under the assumption that the leading process is the exothermic decomposition of the substance in the condensed phase, and the gas-phase processes play a secondary role, is expressed for the most simple case of a reaction of zero order [3, 4, 5], taking (4) and (8) into account by the following formula:

$$u^2 = \frac{2R T_n^2 K_0 \exp(-E/RT_n)}{(1 - \tau_c)^2 Q E} \cdot \frac{K_R K_{HX}}{K_R} \cdot \frac{1 + a K_{HX} p}{1 + a K_{HX} p}; \quad (9)$$

$$T_n = T_0 + \frac{(1 - \tau_c) Q}{c} - \frac{\tau_c Q_c}{c} = T_m - \frac{\tau_c (Q + Q_c)}{c}, \quad (10)$$

where  $\lambda$  - thermal conductivity;

$c$  - specific heat;

$Q$  - decomposition heat;

$Q_c$  - evaporation heat;

$K_0$  - pre-exponent;

$E$  - activation energy;

$T_n$  - temperature of combustion surface;  
 $T_0$  - initial temperature;  
 $T_m$  - maximum temperature,  $a = 1/\rho \cdot m_p$  (considering  $P_c \ll p$ ).

Equations of the material (6) and thermal (10) balances determine the dependence of  $T_n$  on  $p$ .

The pressure coefficient is equal to (it is assumed here that  $K_1$ ,  $K_R$ , and  $K_{HX}$  depend slightly on the temperature  $Q_c = 0$  and  $m_p = m_c$ )

$$\nu = \frac{p \partial u}{u \partial p} = \frac{(T_m - T_n) E}{2 R T_n^2} \left[ 1 + \frac{(T_m - T_n) L}{R T_n^2} \right]^{-1} - \frac{a (K_{HX} - K_R) p}{2(1 + a K_R p)(1 + a K_{HX} p)}, \quad (11)$$

The temperature coefficient

$$\beta = \frac{\partial u}{u \partial T_0} = \left( \frac{E}{2 R T_n^2} + \frac{T_m - T_n}{T_n - T_0} \cdot \frac{L}{R T_n^2} \right) \cdot \frac{\partial T_n}{\partial T_0}, \quad (12)$$

where

$$\frac{\partial T_n}{\partial T_0} = \left[ 1 + \frac{(T_m - T_n) L}{R T_n^2} \right]^{-1}. \quad (13)$$

The dependence of the rate of combustion on pressure is determined by two factors: the equation of the temperature of the combustion surface and the change in concentration of the product accelerating the reaction with an increase in pressure. If the solubility of the products of dissociation in the condensed phase is identical ( $K_R = K_{HX}$ ), then the dependence of  $u$  on  $p$  is determined only by the first factor. If  $K_R > K_{HX}$ , then in a certain region of pressures it is intensified; if  $K_R < K_{HX}$ , then it is weakened and can become opposite in sign ( $\nu < 0$ ).



Figure 1 shows in dimensionless form the dependence of the rate of combustion on pressure with a different relationship between  $K_R$  and  $K_{HX}$  calculated according to formulas

$$\omega^2 = e^{-\varepsilon/\Theta_n} \cdot \frac{K_{HX}}{K_R} \cdot \frac{1 + aK_R \pi}{1 + aK_{HX} \pi}; \quad \pi = \frac{1 - \Theta_0}{1 - \Theta_n} e^{-\kappa/\Theta_n},$$

where

$$\Theta_n = T_n/T_m;$$

$$\pi = p/B;$$

$$\varepsilon = E/RT_m = 10;$$

$$\kappa = L/RT_m = 10;$$

$$\Theta_0 = T_0/T_m = 0.2;$$

$$a K_{HX} = 10^7.$$

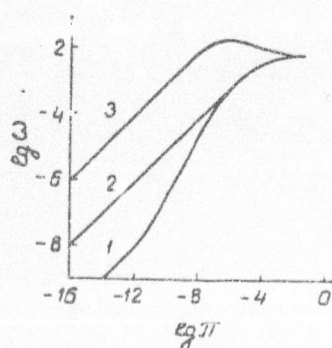


Fig. 1. Dependence of combustion rate on pressure in dimensionless form: 1 -  $K_{HX}/K_R = 10^{-4}$ ; 2 -  $K_{HX}/K_R = 1$ ; 3 -  $K_{HX}/K_R = 10^4$ .

If in the process of thermal decomposition of the substance, products capable of displacing the equilibrium of the initial reaction of transfer of the proton are formed, then they can, by changing the concentration of the product - accelerator of the reaction, have an effect on the combustion rate and its dependence on pressure. Let us assume that the product F (for example,  $H_2O$ ) decreases the concentration of HX according to



It is obvious that

$$[F]_k = K_F RT [F] \sim p.$$

Instead of equation (7), it follows to write

$$[RH^-]_k + [FH^-]_k = [X^-]_k.$$

By using these relations, it is possible to obtain expressions for the concentration of (HX) and combustion rate [6]. In this case the change in the combustion rate and value  $v$  with pressure becomes greater.

If one of the products of decomposition is able to connect R, then the concentration of HX increases, which leads to a corresponding increase in the combustion rate and an increase in  $v$ .

Similarly analyzed are cases when the decomposition is accelerated by the product R, i.e., when

$$w_{y2} = K[R]_k^n.$$

In passing to a comparison of the aforementioned with the experimental data, it is necessary to note that many parameters which enter into the obtained formulas (in the first place, constants of solubility) are unknown at the present time. Nevertheless, the qualitative explanation of the features of combustion of these compounds on the basis of the examined mechanism was important.

It is known that the decomposition of ammonium perchlorate [1], hydrazone perchlorate and diperchlorate [7] and ammonium nitrate [1] is determined by the kinetics of the decomposition of the acid and is accelerated by additions of other acids, whereas the

decomposition of hydrazone nitrate [2] occurs mainly by the decay of hydrazine. The first group of substances corresponds to the scheme examined above.

Regularities of the combustion of ammonium perchlorate are studied in the most detail. Proceeding from data on the vapor pressure of ammonia on the comparison with the vapor pressure of perchloric acid, one should expect that with combustion the solubility of perchloric acid in the condensed phase will be greater, i.e.,  $K_{HX} > K_R$ . Then, according to (9) and (11), with an increase in pressure there should occur a drop in the combustion rate of ammonium perchlorate similar to that of curve 3 of Fig. 1. Experimental data [8, 9] agree with this conclusion. In the region of pressures of 150-400 at a drop in the rate is observed.

It is interesting to note that the combustion of ammonium perchlorate in combustible films [8,10] weakens this drop, which in certain cases is replaced by a plateau. As calculations show [6], this effect is explained in our model. A decrease in the effective heat of reaction leads to the fact that the temperature of the combustion surface varies more greatly with an increase in pressure, and due to this the action of the first factor in formula (11) becomes greater.

With the combustion of perchlorates of organic amines [11, 12], on curves  $u(p)$  regions of the drop in rate or cessation of combustion with the subsequent recommencing of the ability to burn are observed. The mechanism of these phenomena is also apparently connected with the examined effect of kinetic retardation.

Another feature of the process of combustion of these substances consists in the fact that in the region of the drop in rate the combustion acquires an unstable pulsating nature. In



literature there is a number of criteria of the stability of stationary combustion of condensed systems. The most common of them is the criterion of B. V. Novozhilov [13], which is obtained on the basis of an examination of the connection between the combustion rate and the temperature surface and temperature gradient dependent on pressure on the surface of combustion. The combustion mode is stable if

$$\delta = \frac{(k-1)^2}{r(k+1)} < 1, \quad (14)$$

where  $k = (T_n - T_0) \frac{\partial u}{u \partial T_0}$ ;

$$r = \frac{\partial T_n}{\partial T_0} \text{ when } p = \text{const.}$$

The use of (12) and (13) together with (14) leads to the following form of the criterion of stability:

$$\delta = \frac{\left[ \frac{(T_n - T_0) E}{2RT_n^2} - 1 \right]^2}{1 + \frac{(T_n - T_0) E}{2RT_n^2} + \left( T_0 - \frac{Q}{c} - T_n \right) \frac{2L}{RT_n^2}}. \quad (15)$$

The stability of the combustion is increased with an increase in the activation energy  $E$  and decrease in the evaporation  $L$ , i.e., with a decrease in  $v \approx E/2L$ , and also with an increase in the thermal effect of the reaction  $Q$  and initial temperature  $T_0$ .

Equation  $\delta(T_n) = 1$ , which determines the limit of stability, is cubic with respect to  $T_n$  and has three roots, which with definite relationships of the parameters can be real [14] and enter into the region of real values  $T_n$ .

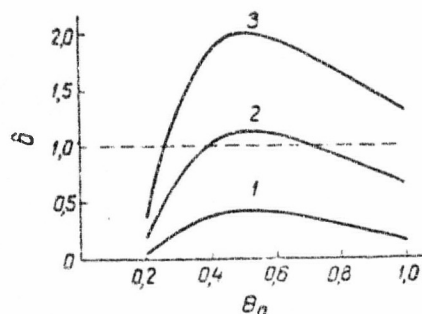


Fig. 2. Dependence of the criterion of stability on the surface temperature of combustion in dimensionless form ( $\kappa = 1$ ;  $\theta_0 = 0.15$ ): 1 -  $\epsilon = 4$ ; 2 -  $\epsilon = 6$ ; 3 -  $\epsilon = 8$ .

Figure 2 shows the dependence of  $\delta$  on the dimensionless temperature  $\theta_n$  for different values of the parameter  $\epsilon = E/RT_m$ . Depending on the magnitude of this parameter, the combustion process can be stable in the whole region of the change in  $T_n$  and, correspondingly,  $p$  (curve 1,  $\delta$  everywhere is less than 1), stable at low and high pressures and unstable in the intermediate region (curve 2, which intersects twice  $\delta = 1$ ) and stable at low pressures (curve 3, which intersects  $\delta = 1$  once). Similar measurements in the nature of the curves causes a decrease in the parameter  $\kappa = L/RT$ . Thus, the relationships determining the combustion stability which result from the examined mechanism are found in a qualitative agreement with the experimental data.

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